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**ATOMIC TRANSPORT AND TRANSFORMATION
BEHAVIOR IN METALLIC GLASSES**



By
Frans Spaepen and David Turnbull

December, 1976

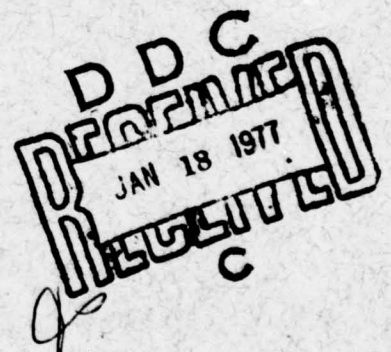
Technical Report No. 1

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Division of Engineering and Applied Physics
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ATOMIC TRANSPORT AND TRANSFORMATION BEHAVIOR IN METALLIC GLASSES

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ABSTRACT

Glasses, metallic or non-metallic, are in states which are configurationally frozen and less stable than some crystallized state. Upon annealing glasses may relax configurationally without transforming and then phase separate and/or crystallize. In this paper we survey the atomic transport behavior in metallic glasses as manifested by their flow, relaxation and transformation behavior. The rate constant for flow, k_{η} , of a glass may be regarded as a product of a "jump" factor and a configurational excitation factor. The activation energy for jumping, or iso-configurational flow, of a metallic glass is only a small fraction, of order 1/10 or less, of the apparent activation energy for flow of the fully relaxed melt in the glass transition range. In configurationally relaxed metallic glasses, the rate constants for phase transformations scale as k_{η} and appear to be controlled by the rate of impurity redistribution. In some configurationally unrelaxed systems, the indicated rates of diffusive transport persist for periods much longer than those expected for configurational relaxation. Some possible explanations for this behavior are discussed.

INTRODUCTION

Amorphous solids, metallic as well as non-metallic, are in states which are configurationally frozen, in large part, and less stable than some crystallized state of the system. Upon annealing, these solids may relax configurationally without crystallization but in holds at longer times or higher temperatures they may phase separate and/or crystallize. The temperatures of configurational freezing, i.e., the glass temperature, T_g , of alloys lie far below the liquiduses, T_l , and typically at $T_{rg}(= T_g/T_l)$ values ranging from 0.45 to 0.65. Thus, to become glasses, alloy melts must be quenched through a wide temperature region of metastability in which the crystal growth rates are extremely high. The necessary conditions for quenching through this metastable regime without crystallization have been specified and discussed in other papers.⁽¹⁻⁵⁾ In this paper, we will survey the atomic transport behavior of glassy metals, as manifested by rates of creep, diffusion, anelastic relaxation, phase separation and crystallization, in and below the temperature range of configurational freezing.

Any of the transport rates alluded to may be considered as a product of a kinetic factor and a factor determined by the thermodynamic driving free energy, ΔG . The kinetic factor will be proportional to some frequency or average of frequencies, $k_1 = 1/\tau$, of the atomic rearrangement characteristic of the transport process. In the glass transition regime the transport rates are all small but the flow rate, from which we may extract the shear viscosity, η , can be measured quite accurately. We shall denote the frequency for viscous flow by $k_\eta = 1/\tau \propto 1/\eta$.

The flow rates of melts drop precipitously, though continuously, with falling temperature in their glass transition ranges. Most models (e.g., free volume, configurational entropy) for this behavior are based on the concept that melt transport requires a highly correlated set of atomic or molecular motions.⁽⁶⁻⁹⁾ It is on the microscopic description of the correlations that the models differ. In any event, the probability of the required correlations should depend strongly on the average atomic or molecular configuration of the system. Indeed, the apparent activation energy for flow of a viscous melt often can be broken into two components. One of these is determined by the change in the equilibrium, or fully relaxed, configuration of the melt with temperature, while the other is the apparent activation energy for flow in a fixed- or iso-configurational state. The experimental procedure for dissociating these components is:

- a) Allow the specimen to reach configurational equilibrium at a temperature T , selected so that the time for thermal equilibration can be made small compared with that for configurational equilibration, and measure the flow rate.
- b) Change the temperature abruptly by δT , and, after thermal equilibration, follow the time dependence of the flow rate. In such experiments, it is often found that the initial flow rate at $T + \delta T$ is not much displaced from its steady value at T . As time progresses, the rate either decreases, if $\delta T < 0$, or increases, if $\delta T > 0$, toward the steady value characteristic of $T + \delta T$ (see schematic in Fig. 1).

Based on these concepts, the rate constant for flow can be described, roughly, in the following terms:

$$k_{\eta} = p_J p_c^*(x_c) \quad (1)$$

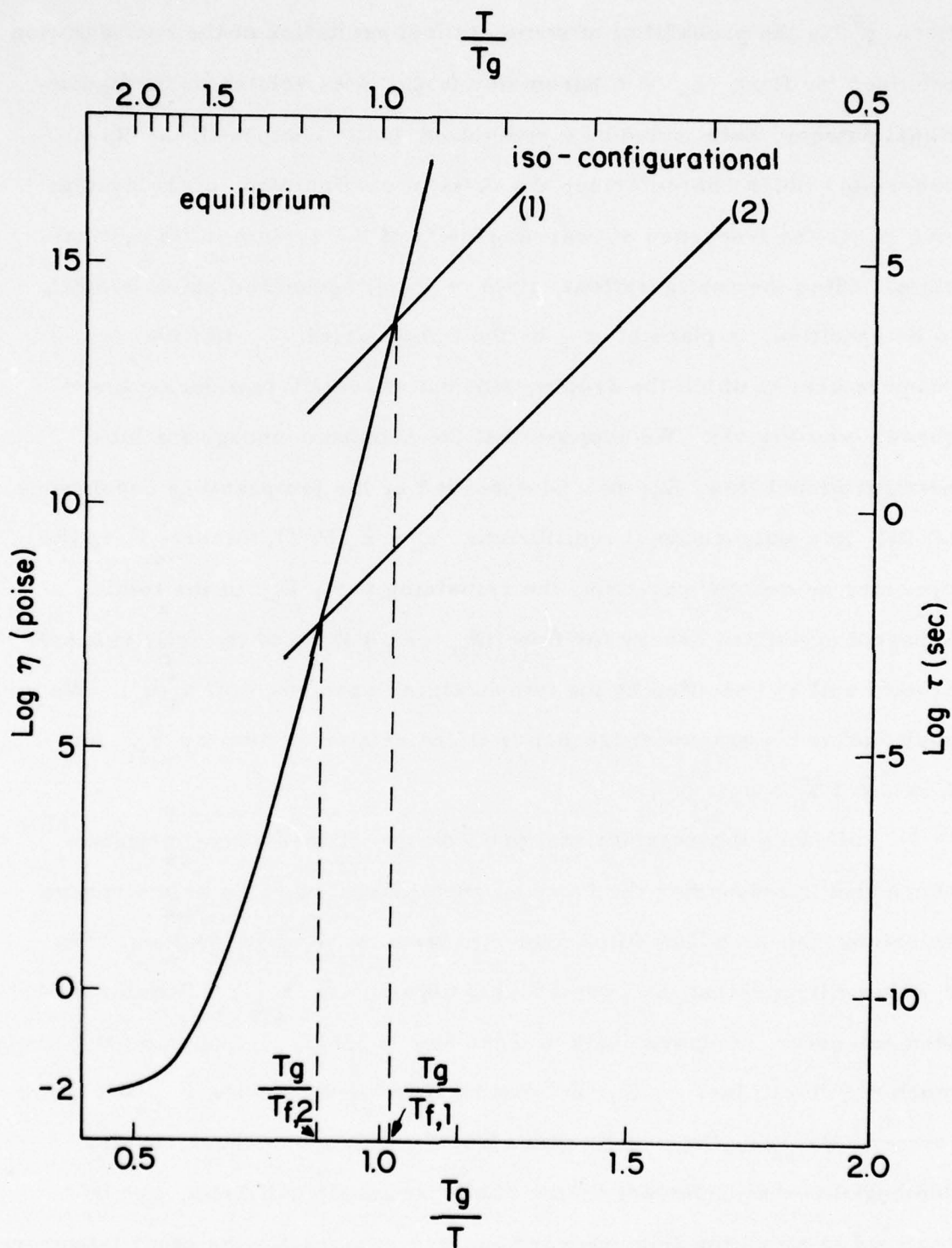


Fig. 1 Schematic representation of the equilibrium and iso-configurational viscosity of an amorphous system. $T_{f,1}$ and $T_{f,2}$ are the fictive temperatures of the configurations corresponding to the iso-configurational viscosities (1) and (2).

Here p_c^* is the probability of some critical excitation of the configuration required for flow, x_c is a parameter (e. g., free volume or configurational entropy, both including a component due to compositional disordering), which characterizes the average configuration of the system and p_J is the frequency of rearrangement of the system in its critical state. Often the configurational state of a melt-quenched glass is taken to be specified, in place of x_c , by the temperature, T_f (fictive temperature) at which the system went out of equilibrium during the quench (see Fig. 1). We suppose that the activation energy for iso-configurational flow, E_J , will be specified by the temperature dependence of p_J . At configurational equilibrium, $x_c = \bar{x}_c(P, T)$, where P is the pressure on the system; thus, the remaining part, E_c , of the total apparent activation energy for flow ($E_\eta = E_J + E_c$) of the fully relaxed system will be specified by the temperature dependence of $p_c^*(\bar{x}_c)$. We shall denote the transport frequency in the related system by \bar{k}_i ; for flow $\bar{k}_i = \bar{k}_\eta = p_J p_c^*(\bar{x}_c)$.

Following the experimental procedures outlined above, Stephens⁽¹⁰⁾ succeeded in measuring the iso-configurational flow rates of amorphous selenium (non-metallic) films over a narrow range of x_c values. His results indicated that E_J was roughly constant at $\sim \frac{1}{3} E$. Similar, but less extensive, measurements of Chen and Turnbull⁽¹¹⁾ indicated relatively much smaller values of E_J , no greater than $\frac{1}{10} E$, for the metallic glass former, $\text{Au}_{77}\text{Si}_{14}\text{Ge}_9$, in its glass transition range. These results demonstrate that departures from configurational equilibrium can be realized at which the flow frequencies, and presumably the other transport frequencies as well, are many orders of magnitude larger or smaller than those of the fully relaxed system at the same temperature and

external pressure. Large stresses, compressive or tensile, within the glass can sharply alter the configurational state, and hence the transport frequencies, of local regions. Such behavior may be especially important in glassy metals, ⁽¹²⁾ formed by rapid melt-quenching or condensation, if the relatively small temperature dependence of iso-configurational flow found for the Au based glasses proves to be a general characteristic of such metals.

The frequencies for the other atomic transport coefficients are not as easily measured in the high viscosity regime as those for flow. Actually, there is considerable evidence ⁽⁹⁾ that the frequencies for self-diffusion, k_D , configurational relaxation, k_c , and crystal growth, k_u all scale as the flow frequency, k_η at least from the low to the intermediate viscosity range of 10^6 to 10^7 poise. Further the rather sketchy existing data suggests that the rough scaling of k_c and k_η extends well into the glass transition range.

The microscopic basis for these scaling relations can be discussed conveniently in terms of the free volume model. ^(6, 7, 9) In this model a critical density attenuation or "hole" is formed in a local region by "random" density fluctuations, i. e. free volume redistribution. A local configuration different from the initial one may then be formed by the collapse of this hole. When a stress is applied, the holes formed should collapse preferentially to those configurations which change the shape of the specimen in accord with the stress bias. We note that this process may lead to diffusive transport as well as to configurational rearrangement and flow. Hence we would expect that k_η , k_D and k_c might scale with each other. However, in a very dense high viscosity system it is

conceivable that a "hole" could exchange with several atoms before collapsing. In this event, the scaling law between k_D and k_η would begin to break down in the direction of k_D falling less rapidly than k_η with decreasing free volume.

Using the conceptual framework just presented, we now survey certain aspects of the flow, diffusive and phase transformation behavior of glassy metals.

CREEP BEHAVIOR

Homogeneous plastic flow, typically at low strain rates, of a glassy metal, around or below T_g is usually referred to as creep. Around T_g , the system is still in configurational equilibrium and, as discussed in the introduction, the steep rise in viscosity with falling temperature is caused by the increasing degree of correlation between the atom motions which contribute to flow. Below T_g , homogeneous plastic flow is only observed at low stresses ($\tau < 10^{-2}$ shear modulus) and low strain rates ($\dot{\gamma} < 10^{-5} \text{ sec}^{-1}$). At higher stresses, glassy metals do not deform homogeneously any more: plastic flow becomes localized in a few very thin shear bands. During this kind of inhomogeneous flow, the material in the shear band is softened, i. e., its structure is different from that of the original material, so that the frequency k_η associated with this flow process cannot simply be compared to that of the other kinetic processes at this temperature. During creep, however, the structure is almost constant, or at least changes sufficiently slowly to allow a comparison of k_η with the frequency associated with other phenomena.

So far, creep experiments below T_g have been reported for only a few glassy metal alloys: $\text{Ni}_{76}\text{P}_{24}$,⁽¹³⁾ $\text{Co}_{75}\text{P}_{25}$,⁽¹³⁾ $\text{Pd}_{80}\text{Si}_{20}$,⁽¹⁴⁾ $\text{Cu}_{60}\text{Zr}_{40}$,⁽¹⁵⁾ and $\text{Fe}_{80}\text{P}_{13}\text{C}_7$.⁽¹⁵⁾ In these experiments, a large fraction of the strain can be recovered after removal of the load. However, after a sufficiently long time, the deformation reaches steady state (i. e., strain rate constant), and it has been shown that the strain produced in this stage of the deformation is totally non-recoverable. In steady state, a shear viscosity $\eta = \tau / \dot{\gamma}$ can be defined. Fig. 2 shows η as a function of temperature for a few glassy metals. For Co_3P , the flow is Newtonian viscous (i. e., η constant for all τ); for Pd_4Si , the viscosity at the lowest stress has been plotted.

Most striking about the temperature dependence of the creep rate in both these systems is the low activation energy E_{Cr} . For Co_3P , $E_{Cr} = 12$ kcal/mole; for Pd_4Si , as plotted in Fig. 2, $E_{Cr} = 8$ kcal/mole. Since the total strain in these creep experiments is at most $\gamma \approx 10^{-3} - 10^{-4}$, and since the strain is roughly equal to the fraction of the atoms that makes a jump which contributes to flow, it seems plausible that the structure of the specimen does not change appreciably during the course of the experiment (for a change in structure, one would expect that almost all atoms have to jump, which corresponds to a straining $\gamma \approx 1$). This means that these creep experiments, if they are done at low enough temperatures where the diffusion is negligible, are iso-configurational processes. As has been pointed out in the introduction, the apparent activation energy $E_J = E_{Cr}$ for such a process is only a fraction of the apparent activation energy, E_η , for flow of the system in configurational equilibrium. A typical value for E_η , (see Fig. 2), is 130 kcal/mole, so

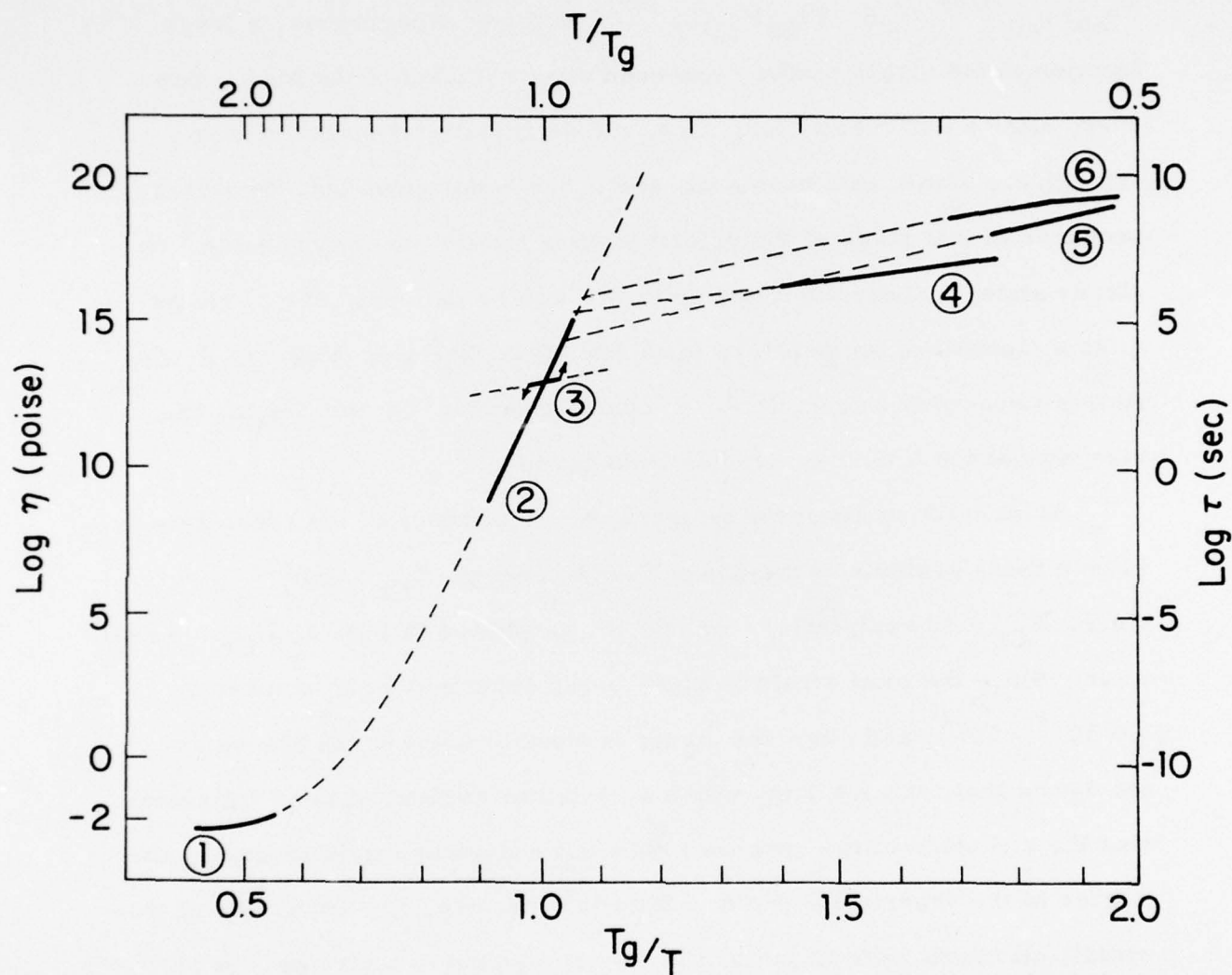


Fig. 2 Flow experiments on some glassy metals: 1) Viscometry on $\text{Au}_{77}\text{Si}_{14}\text{Ge}_9$ (ref. 28). 2) Equilibrium creep in $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ (ref. 29). 3) Iso-configurational creep in $\text{Au}_{77}\text{Si}_{14}\text{Ge}_9$ (ref. 11). 4) Creep in $\text{Pd}_{80}\text{Si}_{20}$ (ref. 14). 5) Creep (1st run) in $\text{Co}_{75}\text{P}_{25}$ (ref. 13). 6) Creep (rerun) in $\text{Co}_{75}\text{P}_{25}$ (ref. 13).

that for these creep experiments $E_{Cr} = E_J \approx E_\eta/10$, which is consistent with Chen and Turnbull's⁽¹¹⁾ estimate of E_J for iso-configurational flow in $Au_{77}Si_{14}Ge_9$.

After the Co_3P samples had been tested at increasing temperatures up to $90^\circ C$, a second set of tests at temperatures below this showed a dramatic decrease (of almost a factor of 10) in the creep rate. The fact that, in Fig. 2, the extrapolation of the creep viscosity to higher temperatures intersects the equilibrium viscosity curve at a higher point for the rerun than for the first run suggests that the structure of the sample in the rerun has relaxed, probably because of the thermal treatment during the test at the highest temperature, towards a different configuration with a higher equilibrium viscosity. In the free volume formulation, this means that the structure has densified on thermal annealing. The creep reruns are then iso-configurational processes in this new structure.

Finally, it is worth noting that the formulation presented in the introduction, which describes the rate constant for flow as a product of a kinetic and a configurational factor, can also be used to describe inhomogeneous flow. In homogeneous flow, the material in the shear bands is softened; in this case, the configurational factor $p_c^*(x_c)$ in the band is set by the external parameters of the flow (e. g., the stress), and not by the intrinsic structural parameters.

TRANSFORMATION BEHAVIOR

Crystal Nucleation in Glass Forming Melts

The necessary conditions for bypassing homogeneous nucleation of crystals in melt quenching have been specified and surveyed in earlier publications. (1-5) Actually the homogeneous nucleation frequency in many non-metallic glass formers, e. g., fused SiO_2 and Se, never reaches measurable levels under any experimentally realizable conditions. Thus, crystallization of these melts and glasses, which exhibit reduced glass temperatures $\bar{T}_{rg} > 2/3$, is always heterogeneously nucleated.

Calculations based on simple nucleation theory, (4) with plausible values (17, 18) assigned to the crystal-melt tension, indicate that homogeneous crystal nucleation also should be imperceptible in those metallic melts in which $\bar{T}_{rg} > 2/3$. At $\bar{T}_{rg} \lesssim 0.6$, the calculated frequencies are large enough to insure copious nucleation at normal cooling rates but, if $0.6 \gtrsim \bar{T}_{rg} \gtrsim 0.45$, not large enough for the occurrence of appreciable crystallization at the very high quench rates $\gtrsim 10^{60} \text{C/sec}$ now available for metal systems.

The reported \bar{T}_{rg} 's of the metallic glass formers are in the range 0.45 to 0.65. Thus, in these alloys, in contrast with the typical non-metallic glass formers, it should be possible to vary widely the density of crystallization centers, and the degree of crystallinity below \bar{T}_{rg} , by adjustment of the rate of quenching to \bar{T}_{rg} . At the highest quench rates, crystallization should be almost completely bypassed. With intermediate quench rates, a partly crystallized structure, consisting of a high number

density of crystallites embedded in an amorphous matrix, may form. When the cooling rate is still lower, crystallization to an actual microcrystalline solid may be virtually complete. The most direct manifestation of this increasing microcrystallinity may be the appearance of sharper detail in the higher diffraction peaks of the interference function.

Certain properties of the partly crystallized alloy may differ rather little from those of the wholly amorphous alloy. For example, the strength and ductility of the alloy might be expected to approximate that of the amorphous matrix provided the crystallites are isolated by this matrix. Indeed, Chou and Spaepen⁽¹⁹⁾ showed that alloys of Pd-Au-Si remained ductile with increasing levels of crystallinity up to 75%.

Evidently the susceptibility of the glassy alloy to crystallization during reheating will increase markedly with the number density, ρ_N , of crystallites formed in the melt quench. As ρ_N increases the temperature, T_{KC} , at which rapid crystallization occurs in reheating decreases. This temperature, often referred to loosely as the "crystallization temperature", is arbitrarily defined. A more proper designation is the "kinetic crystallization temperature", taken to be that at which the crystallization rate attains some specified high value. The large variation of this rate with temperature in the glass transition range leads to the impression that T_{KC} is sharply defined. When ρ_N is negligible T_{KC} may be well above T_g . Its displacement from T_g will decrease as ρ_N increases, and finally, become so small that the glass transition behavior is obscured. In fact, when ρ_N is very large, the morphological evolution of the microstructure during annealing may be like normal grain coarsening rather than nucleation and growth.

Crystal Growth Rates

Under isothermal conditions the frequency, k_u , of crystal growth may be limited (1) by the transport of crystallizing material to the melt-crystal interface and/or (2) by the interfacial process itself. When determined by the former of these steps, k_u should, of course, scale as k_D , the diffusive jump frequency of the crystallizing component in the melt. It may also scale as k_D in a growth process limited by an essential change in compositional short range order in the interfacial region. More generally, k_u should be proportional to k_D whenever crystal growth is controlled by some impurity redistribution process in the melt or glass.⁽⁹⁾

When no impurity redistribution is required, the degree of correlation of the atomic motions effecting crystal growth can be much less than that in configurational change or diffusive transport within the melt or glass. Under these conditions, k_u can be orders of magnitude greater than k_D so that crystals may grow rapidly in the glass at temperatures far below T_g . Indeed, it has been suggested⁽⁹⁾ that in this regime k_u is determined by the collision frequency of atoms from the amorphous phase with the crystal surface.

There have been a number of studies⁽²⁰⁻²³⁾ of the rates of crystallization of configurationally relaxed alloy melts in their glass transition ranges. All these studies showed sigmoidal isotherms, typical of nucleation and growth processes. For a given system, the isotherms differed only by time scaling factors. The time constants decreased sharply as temperature increased, consistent with apparent activation energies equivalent, within the large experimental uncertainties,

to those for viscous flow in the same regime of temperature and alloy composition (see Fig. 3). This behavior indicates that in the fully relaxed amorphous alloy k_u does scale, at least approximately, with k_η . The most plausible interpretation of such scaling is that k_u is determined by a diffusive frequency, k_D , proportional to k_η .

There is evidence that, in some configurationally unrelaxed alloy glasses, crystallization proceeds at temperatures well below T_g with apparent activation energies much below those for flow of the unrelaxed alloys at their T_g . As we have noted, this behavior may be expected if no impurity redistribution attends growth. When limited by such redistribution, growth in glasses frozen in the higher energy configurational states might be rapid initially but it is not easy to see how the high growth rate would persist since extensive configurational relaxation might be expected in the times needed for measurable crystallization. It may be that the crystallization process itself perturbs the configurations in the interfacial regions to states conducive to rapid growth and that, at $T < T_g$, the configurational relaxation rates are too small for the annealing out of these perturbations. One such perturbation, of a gross sort, might develop in amorphous layers between growing crystals owing to tension set up by the decrease in volume on crystallization. According to the free volume model, the isothermal transport rates should be enhanced by the dilatation resulting from the tension. Alternatively, the theory of the "impurity drag" effect, developed for the movement of intercrystalline boundaries, ^(24, 25) may have applicability to the problem discussed here.

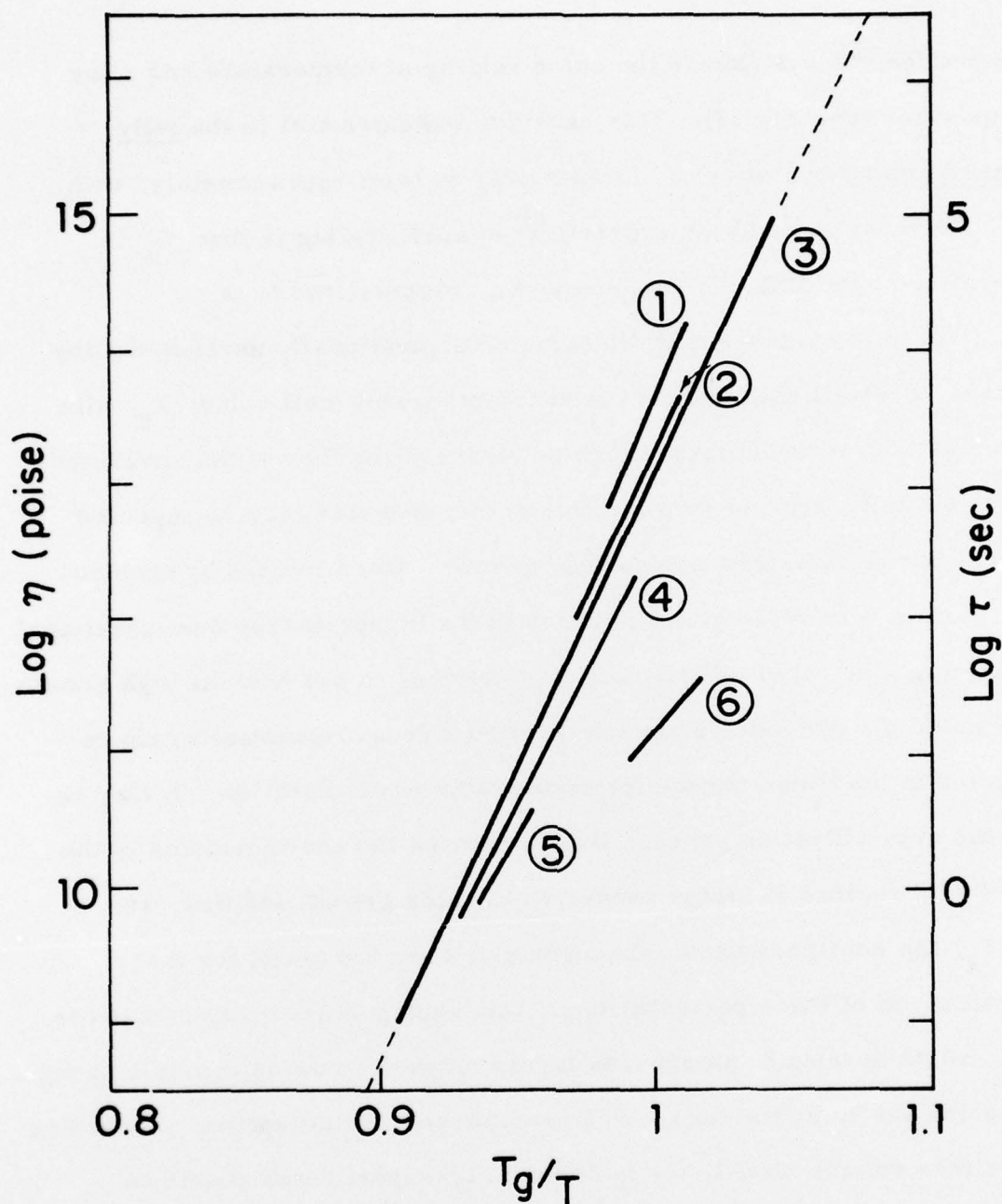


Fig. 3 Time constants for crystallization of some metallic glasses: 1) $\text{Ni}_{75}\text{P}_{16}\text{Al}_3$ (ref. 22) 2) $\text{Pd}_{80}\text{Au}_{3.5}\text{Si}_{16.5}$ (ref. 20). 3) Equilibrium viscosity of $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ (ref. 29). 4) $\text{Pd}_{78.1}\text{Cu}_{5.5}\text{Si}_{16.4}$ (ref. 23) 5) $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ (ref. 21). 6) $\text{Co}_{75}\text{P}_{16}\text{B}_6\text{Al}_3$ (ref. 22).

Phase Separation

Chou and Turnbull presented evidence that the ternary alloy glass $\text{Pd}_{74}\text{Au}_8\text{Si}_{18}$, when heated into the glass transition range, initially phase separates into two viscous melts with different compositions. This process had been indicated by the transmission electron microscopy observations of Chen and Turnbull.⁽²⁶⁾ The conclusions of Chou and Turnbull⁽²⁰⁾ were based on the small and large angle x-ray scattering behavior of much thicker specimens. Their analysis of the time dependence of the process indicated a value, $\sim -3 \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$ for the interdiffusivity in the glass transition range which is within an order of magnitude of that, $\sim -10^{-18}$, predicted by the viscosity scaling relation. This result further supports the conclusion drawn from the studies of the kinetics of crystallization that in the fully relaxed alloy glass the diffusive frequency, k_D scales as that, k_η , for flow.

DIFFUSIVE TRANSPORT

We have noted the evidence from phase transformation behavior that in configurationally relaxed glassy alloys the diffusive transport rates scale as the flow rates. We now consider the problem of diffusion in a glass which is frozen into a high energy configurational state, specified by a fictive temperature, T_f . The initial diffusive frequency at low temperature would fall on an isoconfigurational relation $k_D(T, T_f)$ stemming from the point at T_f on the $\bar{k}_D(T)$ relation. This frequency can be many orders of magnitude greater than the extrapolated value of

$\bar{k}_D(T)$. However, in the normal procedures for measuring diffusivity accurately, many jumps per atom must occur. Therefore, when $k_c \sim k_D$, it appears that diffusion experiments would always yield $k_D = \bar{k}_D$ since configurational relaxation should go virtually to completion in their earliest stages.

From this viewpoint, the results of Gupta, Tu and Asai⁽²⁷⁾ (see Fig. 4) on the diffusivity of radio-silver into $\text{Pd}_{81}\text{Si}_{19}$ are surprising. We note that their $k_D (= 1/\tau_D)$ values are, at temperatures much below T_g , many orders of magnitude greater than the extrapolated $\bar{k}_D(T)$ and indicate a fictive temperature at which $\eta \sim 10^7$ poise. We expect that Ag should model, at least roughly, the siting and transport behavior of Pd, the major constituent of the alloy. Thus, the results of Gupta et al. imply that extensive transport of the major element can occur below T_g without appreciable configurational relaxation, i. e., $k_D \gg k_c$. To test this implication, k_c , as indicated by the volume relaxation rate, should be measured under the conditions of the diffusion experiments. A difference between k_D and k_c might be explained if diffusion below T_g occurs by the movement of discrete vacancies and volume relaxation by the collapse of the excess number of these vacancies. Then, if a vacancy jumped many times before collapsing, k_D could, indeed, be much larger than either k_c or k_η , since both configurational relaxation and flow would be effected only by the collapse of voids. Theoretical evaluation of this possibility would be quite difficult.

Another possible interpretation of the Gupta et al. results is that full configurational relaxation at $T \ll T_g$ is retarded because of configurational heterogeneity, on a spatial scale of $\sim 10^2$ to 10^4 atom

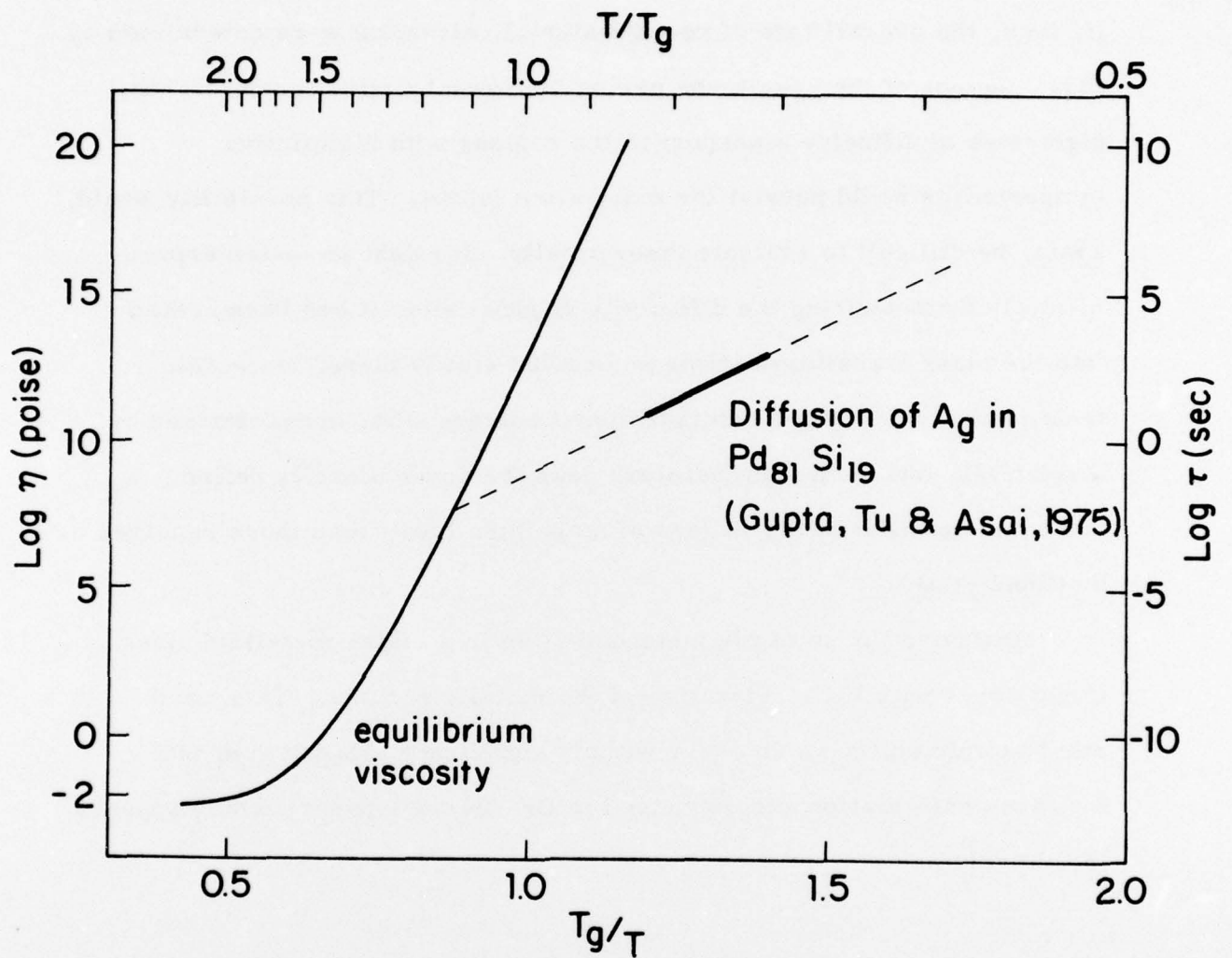


Fig. 4 Equilibrium viscosity of metallic glasses (schematic) and the time constants for diffusion of Ag¹¹⁰ in Pd₈₁Si₁₉ (ref. 27).

spacings, which might arise from quenching non-uniformities at the high quench rates. This state might be characterized, for example, by some distribution of fictive temperatures over the volume of the specimen. If, then, the overall rate of configurational relaxation were determined by those regions of the specimens having the lowest fictive temperatures, high rates of diffusive transport in the regions with high fictive temperatures could persist for many atom jumps. This possibility would, again, be difficult to evaluate theoretically. It might be tested experimentally by measuring the diffusivity of glass after it had been heated into the glass transition regime and cooled slowly therefrom. This treatment should lead to configurational homogeneity, characterized by a relatively low fictive temperature near the conventionally defined T_g , and hence to diffusivities orders of magnitude lower than those reported by Gupta et al.

Diffusive jumps of the metalloid atom in a metal-metalloid glass might occur with little relaxation of the metal structure. These and other atomic shifts which occur without significant relaxation of the average configuration are discussed in Dr. Berry's paper, which appears in this volume.

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